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<p>(51) International Patent Classification ⁷ : C08F 210/06, 210/16</p>	<p>A1</p>	<p>(11) International Publication Number: WO 00/37514 (43) International Publication Date: 29 June 2000 (29.06.00)</p>
<p>(21) International Application Number: PCT/US99/29787 (22) International Filing Date: 15 December 1999 (15.12.99) (30) Priority Data: 60/113,227 21 December 1998 (21.12.98) US (71) Applicant: EXXON CHEMICAL PATENTS INC. [US/US]; 5200 Bayway Dr., Baytown, TX 77520-5200 (US). (72) Inventors: MARKEL, Eric, J.; 4534 Natural Bridge Drive, Kingwood, TX 77345 (US). WENG, Weiqing; 13707 Shadow Falls Court, Houston, TX 77059 (US). DEK- MEZIAN, Armenag, H.; 2806 Evergreen Cliff Trail, King- wood, TX 77345 (US). (74) Agents: MULLER, William, G. et al.; Exxon Chemical Company, P.O. Box 2149, Baytown, TX 77522-2149 (US).</p>	<p>(81) Designated States: BR, CA, CN, JP, KR, MX, SG, European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). Published <i>With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i></p>	
<p>(54) Title: BRANCHED SEMI-CRYSTALLINE ETHYLENE-PROPYLENE COMPOSITIONS (57) Abstract <p>Branched ethylene-propylene compositions which have improved melt strength and shear thinning are provided. The weight average branching index g' for the higher molecular weight region of the ethylene-propylene composition is less than 0.95. Additionally, a novel process is provided for efficiently producing a branched ethylene-propylene composition comprising: a) contacting propylene monomers and ethylene monomers in a reactor with an inert hydrocarbon solvent or diluent and a catalyst composition comprising one or more single site catalyst compounds.</p></p>		

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BRANCHED SEMI-CRYSTALLINE ETHYLENE-PROPYLENE COMPOSITIONS**FIELD OF THE INVENTION**

5 The present invention relates to gel-free, diene-free, branched semi-crystalline high-C₃ ethylene-propylene compositions and a method for the preparation of branched semi-crystalline high-C₃ ethylene-propylene compositions utilizing single site catalyst compounds.

BACKGROUND OF THE INVENTION

10 The class of rubbery ethylene-propylene copolymers, conventionally referred to as EPR polymers, is well known and has gained substantial commercial acceptance. The copolymers are known to have good properties such as weatherability, ozone resistance and thermal stability and the polymers have
15 accepted utility in automotive applications, as construction materials and as wire and cable coatings, among others. However, conventional ethylene-propylene rubbery copolymers are often difficult to process unless compounded by relatively large amounts of other materials.

 A number of proposals have been made to improve the processability of
20 the ethylene-propylene rubbery copolymer. In Yamamoto et al, U.S. Pat. No. 4,125,699, there are disclosed ethylene-propylene copolymers having a relatively high ethylene content produced in the presence of vanadium-containing polymerization catalysts. The copolymers of Yamamoto et al. are said to have improved processability because of a relatively broad molecular weight
25 distribution. Vanadium catalysts, however, are of relatively low activity and many, if not most, of the more recent commercial ethylene-propylene rubbery copolymers are produced with a titanium-based catalyst because of the higher catalytic activity available through the use of such catalysts.

 Processability has been improved in other types of polymers due to the
30 presence of long chain branching. For example, EP 190 889 A2 discloses high energy irradiation of polypropylene to create what is believed to be polypropylene having substantial free-end long branches of propylene units. EP 384 431

discloses the use of peroxide decomposition of polypropylene in the substantial absence of oxygen to obtain a similar product.

Other examples of long chain branched polypropylene include U.S. Patent 5,541,236, which introduces long chain branching by bridging two PP backbones to form H-type polymers, and U.S. Patent 5,514,761, which uses dienes incorporated in the backbones to achieve a similar effect. However, it is difficult to avoid cross-linking and gel formation in such processes.

Thus, there is still a need for ethylene-propylene copolymer compositions having improved processability.

SUMMARY OF THE INVENTION

The present invention meets that need by providing gel-free, diene-free, branched ethylene-propylene (EP) compositions which have improved sprayability, elasticity and molecular weight. The weight average branching index g' for the higher molecular weight region of the ethylene-propylene compositions is less than 0.95. Additionally, a novel process is provided for efficiently producing a branched ethylene-propylene composition comprising:

- a) contacting propylene monomers and ethylene monomers in a reactor with an inert hydrocarbon solvent or diluent and a catalyst composition comprising one or more single site catalyst compounds capable of producing an ethylene-propylene polymer at a temperature from about 50°C to about 180°C, wherein the ratio in the reactor of the propylene and ethylene monomers to the inert hydrocarbon solvent or diluent is less than 2.0, and further, wherein the propylene and ethylene monomers and the inert hydrocarbon solvent or diluent comprise no more than 90 percent of the total contents of the reactor; and
- b) recovering a branched ethylene-propylene composition, wherein the weight average branching index g' for the higher molecular

weight region of the ethylene-propylene composition is less than 0.95.

DETAILED DESCRIPTION OF THE INVENTION

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The present invention provides a novel method for producing gel-free, diene-free, branched EP. In addition, the branched EP product of the present invention is novel. The weight average branching index g' for the higher molecular weight region of the ethylene-propylene composition is less than 0.95. Preferably, the weight average branching index g' for the higher molecular weight region of the ethylene-propylene composition is less than 0.90. More preferably, it is less than 0.85. These branching characteristics result in a polymer with improved rheological characteristics.

An unusual feature of the branched ethylene-propylene of the present invention is the presence of a significant amount of branching in the higher molecular weight range of the polymer. This branching results in improved melt strength and shear thinning, as well as other unique physical properties. In this case, the amount of branching is determined using the weight average branching index g' of the branched ethylene-propylene. The weight average branching index g' is defined as $g' = [IV]_{br}/[IV]_{lin|_{Mw}}$ wherein $[IV]_{br}$ is the intrinsic viscosity of a branched polymer sample and $[IV]_{lin}$ is the intrinsic viscosity of a linear polymer sample. It is well known in the art that as the g' value decreases, branching increases. See B.H. Zimm and W.H. Stockmayer, J. Chem. Phys. 17, 1301 (1949).

25 With regard to the molecular weight distribution of the ethylene-propylene composition of the present invention, the following definitions apply:

Lower molecular weight region: That portion of the polymer product which has a molecular weight which is less than Peak MW (M_p).

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Higher molecular weight region: That portion of the polymer product which has a molecular weight which is more than Peak MW (M_p).

Preferably, the ethylene-propylene polymers of the present invention have a high propylene content, wherein a majority of the monomeric content of the polymer is propylene. In other words, the propylene content of the ethylene-propylene polymers is greater than 50%. More preferably, the propylene content of the ethylene-propylene polymers is in the range of 75 to 95%. Most preferably, the propylene content of the ethylene-propylene polymers is in the range of 80 to 90%.

Other comonomers can be included in the branched ethylene-propylene of the present invention. Examples of these other comonomers include C_4 - C_{20} α -olefins, geminally disubstituted monomers, C_5 - C_{25} cyclic olefins, C_8 - C_{25} styrenic olefins, and lower carbon number (C_3 - C_8) alkyl substituted analogs of the cyclic and styrenic olefins. Preferably, the other comonomers comprise from 3 to 25 mole percent of the ethylene-propylene composition. More preferably, they comprise from 5 to 20 mole percent of the ethylene-propylene composition.

In a preferred embodiment, the total comonomer content of the branched ethylene-propylene composition of the present invention is from 5 to 40 mole percent. More preferably, the total comonomer content is from 10 to 30 mole percent. Most preferably, the total comonomer content is from 15 to 25 mole percent.

Catalysts

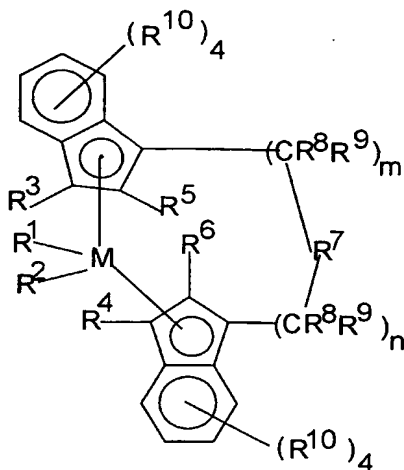
Catalysts which are useful for producing the branched EP of the present invention include single-site catalysts which are capable of producing ethylene-propylene polymers. Single-site catalysts which are useful in the present invention include metallocene catalysts, as well as complexes such as those described in Johnson, Killian, and Brookhart, *J. Am. Chem. Soc.*, **1995**, *117*, 6414; Small, Brookhart and Bennett, *J. Am. Chem. Soc.*, **1998**, *120*, 4049-4050;

Repo et al., *Journal of Organometallic Chemistry*, 1997, 549, 177-186; and Britovsek et al., *Chem. Commun.*, 1998, 849-850. Other useful single-site catalysts include bridged bis(arylamido) Group 4 compounds such as those described by D. H. McConville, *et al*, in *Organometallics* 1995, 14, 5478-5480. Each of these documents is incorporated by reference for the purposes of U.S. patent practice.

Preferably, metallocene catalysts are used to produce the branched ethylene-propylene of the present invention. As used herein, "metallocene" refers generally to compounds represented by the formula $Cp_mMR_nX_q$ wherein Cp is a cyclopentadienyl ring which may be substituted, or derivative thereof which may be substituted, M is a Group 4, 5, or 6 transition metal, for example titanium, zirconium, hafnium, vanadium, niobium, tantalum, chromium, molybdenum and tungsten, R is a hydrocarbyl group or hydrocarboxy group having from one to 20 carbon atoms, X is a halogen, and $m=1-3$, $n=0-3$, $q=0-3$, and the sum of $m+n+q$ is equal to the oxidation state of the transition metal.

Methods for making and using metallocenes are well known in the art. For example, metallocenes are detailed in United States Patent Nos. 4,530,914; 4,542,199; 4,808,561; 4,871,705; 4,892,851; 4,933,403; 4,937,299; 5,017,714; 5,057,475; 5,120,867; 5,132,381; 5,155,080; 5,198,401; 5,278,119; 5,304,614; 5,324,800; 5,350,723; and 5,391,790 each fully incorporated herein by reference.

Preferred metallocenes are those that are stereorigid and comprise a Group 4, 5, or 6 transition metal, biscyclopentadienyl derivative, preferably bis-indenyl metallocene components having the following general structure:



wherein M^1 is a metal of Group 4, 5, or 6 of the Periodic Table, for example titanium, zirconium, hafnium, vanadium, niobium, tantalum, chromium, molybdenum and tungsten, preferably, zirconium, hafnium and titanium, most preferably zirconium and hafnium;

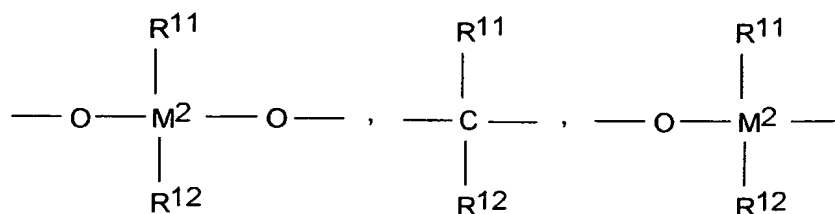
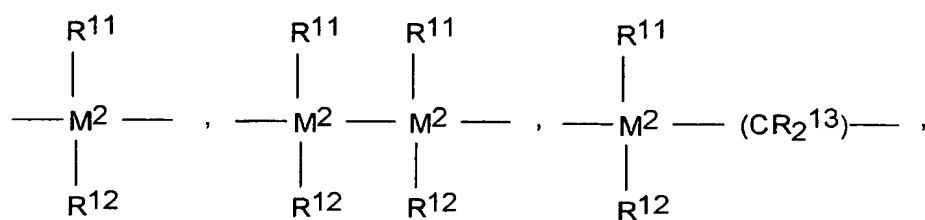
R^1 and R^2 are identical or different, are one of a hydrogen atom, a C_1 - C_{10} alkyl group, preferably a C_1 - C_3 alkyl group, a C_1 - C_{10} alkoxy group, preferably a C_1 - C_3 alkoxy group, a C_6 - C_{10} aryl group, preferably a C_6 - C_8 aryl group, a C_6 - C_{10} aryloxy group, preferably a C_6 - C_8 aryloxy group, a C_2 - C_{10} alkenyl group, preferably a C_2 - C_4 alkenyl group, a C_7 - C_{40} arylalkyl group, preferably a C_7 - C_{10} arylalkyl group, a C_7 - C_{40} alkylaryl group, preferably a C_7 - C_{12} alkylaryl group, a C_8 - C_{40} arylalkenyl group, preferably a C_8 - C_{12} arylalkenyl group, or a halogen atom, preferably chlorine;

R^3 and R^4 are hydrogen atoms;

R^5 and R^6 are identical or different, preferably identical, are one of a hydrogen atom, halogen atom, preferably a fluorine, chlorine or bromine atom, a C_1 - C_{10} alkyl group, preferably a C_1 - C_4 alkyl group, which may be halogenated, a C_6 - C_{10} aryl group, which may be halogenated, preferably a C_6 - C_8 aryl group, a C_2 - C_{10} alkenyl group, preferably a C_2 - C_4 alkenyl group, a C_7 - C_{40} -arylalkyl group, preferably a C_7 - C_{10} arylalkyl group, a C_7 - C_{40} alkylaryl group, preferably

a C₇-C₁₂ alkylaryl group, a C₈-C₄₀ arylalkenyl group, preferably a C₈-C₁₂ arylalkenyl group, a -NR¹⁵, -SR¹⁵, -OR¹⁵, -OSiR₃¹⁵ or -PR₂¹⁵ radical, wherein R¹⁵ is one of a halogen atom, preferably a chlorine atom, a C₁-C₁₀ alkyl group, preferably a C₁-C₃ alkyl group, or a C₆-C₁₀ aryl group, preferably a C₆-C₉ aryl group;

R⁷ is



=BR¹¹, =AIR¹¹, -Ge-, -Sn-, -O-, -S-, =SO, =SO₂, =NR¹¹, =CO, PR¹¹, or =P(O)R¹¹;

wherein:

R¹¹, R¹² and R¹³ are identical or different and are a hydrogen atom, a halogen atom, a C₁-C₂₀ alkyl group, preferably a C₁-C₁₀ alkyl group, a C₁-C₂₀ fluoroalkyl group, preferably a C₁-C₁₀ fluoroalkyl group, a C₆-C₃₀ aryl group, preferably a C₆-C₂₀ aryl group, a C₆-C₃₀ fluoroaryl group, preferably a C₆-C₂₀ fluoroaryl group, a C₁-C₂₀ alkoxy group, preferably a C₁-C₁₀ alkoxy group, a C₂-C₂₀ alkenyl group, preferably a C₂-C₁₀ alkenyl group, a C₇-C₄₀ arylalkyl group, preferably a C₇-C₂₀ arylalkyl group, a C₈-C₄₀ arylalkenyl group,

preferably a C₈-C₂₂ arylalkenyl group, a C₇-C₄₀ alkylaryl group, preferably a C₇-C₂₀ alkylaryl group or R¹¹ and R¹², or R¹¹ and R¹³, together with the atoms binding them, can form ring systems;

M² is silicon, germanium or tin, preferably silicon or germanium, most preferably silicon;

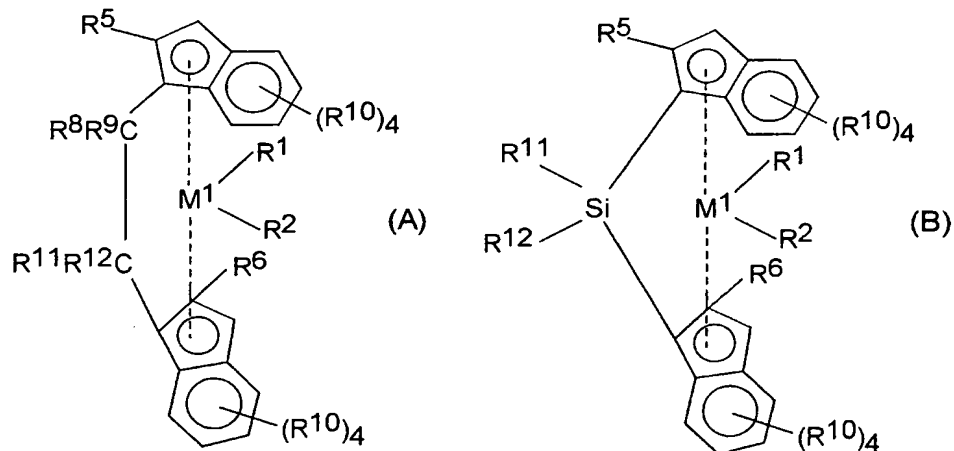
R⁸ and R⁹ are identical or different and have the meanings stated for R¹¹;

m and n are identical or different and are zero, 1 or 2, preferably zero or 1, m plus n being zero, 1 or 2, preferably zero or 1; and

the radicals R¹⁰ are identical or different and have the meanings stated for R¹¹, R¹² and R¹³. Two adjacent R¹⁰ radicals can be joined together to form a ring system, preferably a ring system containing from about 4-6 carbon atoms.

Alkyl refers to straight or branched chain substituents. Halogen (halogenated) is fluorine, chlorine, bromine or iodine atoms, preferably fluorine or chlorine.

Particularly preferred metallocenes are compounds of the structures:



wherein:

M^1 is Zr or Hf, R^1 and R^2 are methyl or chlorine, and R^5 , R^6 , R^8 , R^9 , R^{10} , R^{11} and R^{12} have the above-mentioned meanings.

The chiral metallocenes may be used as a racemate for the preparation of highly isotactic polypropylene polymers and copolymers. It is also possible to use the pure R or S form. An optically active polymer can be prepared with these pure stereoisomeric forms. Preferably the meso form of the metallocene is removed to ensure the center (i.e., the metal atom) provides stereoregular polymerization. Separation of the stereoisomers can be accomplished by known literature techniques. For special products it is also possible to use rac/meso mixtures.

Methods for preparing metallocenes of the present invention are fully described in the Journal of Organometallic Chem., volume 288, (1958), pages 63-67, and in EP-A- 320762, for preparation of the metallocenes described, both of which are herein fully incorporated by reference.

Illustrative but non-limiting examples of some preferred metallocenes include: Dimethylsilanylbis (2-methyl-4-phenyl-1-indenyl)ZrCl₂

Dimethylsilanylbis(2-methyl-4,5-benzoindenyl)ZrCl₂;

Dimethylsilanylbis(2-methyl-4,6-diisopropylindenyl)ZrCl₂;

Dimethylsilanylbis(2-ethyl-4-phenyl-1-indenyl)ZrCl₂;

Dimethylsilanylbis (2-ethyl-4-naphthyl-1-indenyl)ZrCl₂,

Phenyl(Methyl)silanylbis(2-methyl-4-phenyl-1-indenyl)ZrCl₂,

Dimethylsilanylbis(2-methyl-4-(1-naphthyl)-1-indenyl)ZrCl₂,

Dimethylsilanylbis(2-methyl-4-(2-naphthyl)-1-indenyl)ZrCl₂,

Dimethylsilanylbis(2-methyl-indenyl)ZrCl₂,

Dimethylsilanylbis(2-methyl-4,5-diisopropyl-1-indenyl)ZrCl₂,

Dimethylsilanylbis(2,4,6-trimethyl-1-indenyl)ZrCl₂,

Phenyl(Methyl)silanylbis(2-methyl-4,6-diisopropyl-1-indenyl)ZrCl₂,

1,2-Ethandiylbis(2-methyl-4,6-diisopropyl-1-indenyl)ZrCl₂,

1,2-Butandiylbis(2-methyl-4,6-diisopropyl-1-indenyl)ZrCl₂,

Dimethylsilanylbis(2-methyl-4-ethyl-1-indenyl)ZrCl₂,

Dimethylsilanylbis(2-methyl-4-isopropyl-1-indenyl)ZrCl₂,
Dimethylsilanylbis(2-methyl-4-t-butyl-1-indenyl)ZrCl₂,
Phenyl(Methyl)silanylbis(2-methyl-4-isopropyl-1-indenyl)ZrCl₂,
Dimethylsilanylbis(2-ethyl-4-methyl-1-indenyl)ZrCl₂,
5 Dimethylsilanylbis(2,4-dimethyl-1-indenyl)ZrCl₂,
Dimethylsilanylbis(2-methyl-4-ethyl-1-indenyl)ZrCl₂,
Dimethylsilanylbis(2-methyl- α -acenaphth-1-indenyl)ZrCl₂,
Phenyl(Methyl)silanylbis(2-methyl-4,5-benzo-1-indenyl)ZrCl₂,
Phenyl(Methyl)silanylbis(2-methyl-4,5-(methylbenzo)-1-indenyl)ZrCl₂,
10 Phenyl(Methyl)silanylbis(2-methyl-4,5-(tetramethylbenzo)-1-indenyl)ZrCl₂,
Phenyl(Methyl)silanylbis(2-methyl-a-acenaphth-1-indenyl)ZrCl₂,
1,2-Ethandiylbis(2-methyl-4,5-benzo-1-indenyl)ZrCl₂,
1,2-Butandiylbis(2-methyl-4,5-benzo-1-indenyl)ZrCl₂,
Dimethylsilanylbis(2-methyl-4,5-benzo-1-indenyl)ZrCl₂,
15 1,2-Ethandiylbis(2,4,7-trimethyl-1-indenyl)ZrCl₂,
Dimethylsilanylbis(2-methyl-1-indenyl)ZrCl₂,
1,2-Ethandiylbis(2-methyl-1-indenyl)ZrCl₂,
Phenyl(Methyl)silanylbis(2-methyl-1-indenyl)ZrCl₂,
Diphenylsilanylbis(2-methyl-1-indenyl)ZrCl₂,
20 1,2-Butandiylbis(2-methyl-1-indenyl)ZrCl₂,
Dimethylsilanylbis(2-ethyl-1-indenyl)ZrCl₂,
Dimethylsilanylbis(2-methyl-5-isobutyl-1-indenyl)ZrCl₂,
Phenyl(Methyl)silanylbis(2-methyl-5-isobutyl-1-indenyl)ZrCl₂,
Dimethylsilanylbis(2-methyl-5-t-butyl-1-indenyl)ZrCl₂,
25 Dimethylsilanylbis(2,5,6-trimethyl-1-indenyl)ZrCl₂, and the like.

Some preferred metallocene catalyst components are described in detail in U.S. Patent Nos. 5,149,819, 5,243,001, 5,239,022, 5,296,434 and 5,276,208 all of which are herein fully incorporated by reference. In addition, the bis-amido and
30 bis-arylamido transition metal catalysts of U.S. patent 5,318,935 and copending

U.S. patent application 08/ 803,687, filed 2/24/97, can be useful in forming the branched ethylene-propylene of the present invention.

Most preferably, the catalyst used to produce the branched ethylene-propylene of the present invention is a substituted bridged bis-indenyl zirconocene or hafnocene such as dimethylsilyl bis(2-methyl-indenyl) ZrCl₂, dimethylsilyl bis(2-methyl-indenyl) ZrMe₂, dimethylsilyl bis(2-methyl-4-phenyl-1-indenyl) ZrCl₂, dimethylsilyl bis(2-methyl-4-(1-naphthyl)-1-indenyl) ZrCl₂, or dimethylsilyl bis(indenyl)hafnium dimethyl.

The terms "cocatalyst" and "activator" are used herein interchangeably and are defined to be any compound or component which can activate a bulky ligand transition metal compound or a metallocene, as defined above. Alumoxane may be used as an activator. There are a variety of methods for preparing alumoxane, non-limiting examples of which are described in U.S. Patent No. 4,665,208, 4,952,540, 5,091,352, 5,206,199, 5,204,419, 4,874,734, 4,924,018, 4,908,463, 4,968,827, 5,308,815, 5,329,032, 5,248,801, 5,235,081, 5,157,137, 5,103,031 and EP-A-0 561 476, EP-B1-0 279 586, EP-A-0 594-218 and WO 94/10180, each of which is fully incorporated herein by reference. It may be preferable to use a visually clear methylalumoxane. A cloudy or gelled alumoxane can be filtered to produce a clear solution or clear alumoxane can be decanted from the cloudy solution.

It is also within the scope of this invention to use ionizing activators, neutral or ionic, or compounds such as tri(n-butyl)ammonium tetrakis(pentafluorophenyl)boron, which ionize the neutral metallocene compound. Such ionizing compounds may contain an active proton, or some other cation associated with but not coordinated or only loosely coordinated to the remaining ion of the ionizing compound. Combinations of activators are also contemplated by the invention, for example, alumoxane and ionizing activators in combinations, see for example, WO 94/07928.

Descriptions of ionic catalysts for coordination polymerization comprised of metallocene cations activated by non-coordinating anions appear in the early work in EP-A-0 277 003, EP-A-0 277 004 and US patent 5,198,401 and WO-A-

92/00333 (incorporated herein by reference). These teach a preferred method of preparation wherein metallocenes (bisCp and monoCp) are protonated by an anion precursor such that an alkyl/hydride group is abstracted from a transition metal to make it both cationic and charge-balanced by the non-coordinating anion.

5 The term "noncoordinating anion" means an anion which either does not coordinate to said cation or which is only weakly coordinated to said cation thereby remaining sufficiently labile to be displaced by a neutral Lewis base. "Compatible" noncoordinating anions are those which are not degraded to neutrality when the initially formed complex decomposes. Further, the anion will
10 not transfer an anionic substituent or fragment to the cation so as to cause it to form a neutral four coordinate metallocene compound and a neutral by-product from the anion. Noncoordinating anions useful in accordance with this invention are those which are compatible, stabilize the metallocene cation in the sense of balancing its ionic charge in a +1 state, yet retain sufficient lability to permit
15 displacement by an ethylenically or acetylenically unsaturated monomer during polymerization.

 The use of ionizing ionic compounds not containing an active proton but capable of producing both the active metallocene cation and a noncoordinating anion is also known. See, EP-A-0 426 637 and EP-A- 0 573 403 (incorporated
20 herein by reference). An additional method of making the ionic catalysts uses ionizing anion pre-cursors which are initially neutral Lewis acids but form the cation and anion upon ionizing reaction with the metallocene compounds, for example the use of tris(pentafluorophenyl) boron. See EP-A-0 520 732 (incorporated herein by reference). Ionic catalysts for addition polymerization
25 can also be prepared by oxidation of the metal centers of transition metal compounds by anion pre-cursors containing metallic oxidizing groups along with the anion groups, see EP-A-0 495 375 (incorporated herein by reference).

 Where the metal ligands include halogen moieties (for example, bis-cyclopentadienyl zirconium dichloride) which are not capable of ionizing
30 abstraction under standard conditions, they can be converted via known alkylation reactions with organometallic compounds such as lithium or aluminum hydrides

or alkyls, alkylalumoxanes, Grignard reagents, etc. See EP-A-0 500 944 and EP-A1-0 570 982 (incorporated herein by reference) for *in situ* processes describing the reaction of alkyl aluminum compounds with dihalo-substituted metallocene compounds prior to or with the addition of activating anionic compounds.

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Support Materials

The metallocenes described herein may be supported using a porous particulate material, such as for example, talc, inorganic oxides, inorganic chlorides and resinous materials such as polyolefin or polymeric compounds.

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Preferred support materials are porous inorganic oxide materials, which include those from the Periodic Table of Elements of Groups 2, 3, 4, 5, 13 or 14 metal oxides. Silica, alumina, silica-alumina, and mixtures thereof are particularly preferred. Other inorganic oxides that may be employed either alone or in combination with the silica, alumina or silica-alumina are magnesia, titania, zirconia, and the like.

15

Preferably the support material is porous silica which has a surface area in the range of from about 10 to about 700 m²/g, a total pore volume in the range of from about 0.1 to about 4.0 cc/g and an average particle size in the range of from about 10 to about 500 μm. More preferably, the surface area is in the range of from about 50 to about 500 m²/g, the pore volume is in the range of from about 0.5 to about 3.5 cc/g and the average particle size is in the range of from about 20 to about 200 μm. Most preferably the surface area is in the range of from about 100 to about 400 m²/g, the pore volume is in the range of from about 0.8 to about 3.0 cc/g and the average particle size is in the range of from about 30 to about 100 μm. The average pore size of typical porous support materials is ≤ 10Å. Preferably, a support material is used that has an average pore diameter of ≤ 50Å, and most preferably it is in the range of from about 75 to about 350Å. It may be particularly desirable to dehydrate the silica at a temperature of from about 100°C to about 800°C anywhere from about 3 to about 24 hours.

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The metallocenes, activator and support material may be combined in any number of ways. Suitable support techniques are described in U. S Patent Nos. 4,808,561 and 4,701,432 (each fully incorporated herein by reference.) Preferably the metallocenes and activator are combined and their reaction product supported on the porous support material as described in U. S. Patent No. 5,240,894 and WO 94/ 28034, WO 96/00243, and WO 96/00245 (each fully incorporated herein by reference.) Alternatively, the metallocenes may be preactivated separately and then combined with the support material either separately or together. If the metallocenes are separately supported, then preferably, they are dried then combined as a powder before use in polymerization.

Regardless of whether the metallocene and activator are separately precontacted or whether the metallocene and activator are combined at once, the total volume of reaction solution applied to porous support is preferably less than about 4 times the total pore volume of the porous support, more preferably less than about 3 times the total pore volume of the porous support and even more preferably in the range of from more than about 1 to less than about 2.5 times the total pore volume of the porous support. Procedures for measuring the total pore volume of porous support are well known in the art. The preferred method is described in Volume 1, *Experimental Methods in Catalyst Research*, Academic Press, 1968, pages 67-96.

Methods of supporting ionic catalysts comprising metallocene cations and noncoordinating anions are described in WO 91/09882, WO 94/03506, WO 96/04319 and U.S. patent 5,643,847 (incorporated herein by reference.) The methods generally comprise either physical adsorption on traditional polymeric or inorganic supports that have been largely dehydrated and dehydroxylated, or using neutral anion precursors that are sufficiently strong Lewis acids to activate retained hydroxy groups in silica containing inorganic oxide supports such that the Lewis acid becomes covalently bound and the hydrogen of the hydroxy group is available to protonate the metallocene compounds.

The supported catalyst system may be used directly in polymerization or the catalyst system may be prepolymerized using methods well known in the art. For details regarding prepolymerization, see United States Patent Nos. 4,923,833 and 4,921,825, EP 0 279 863 and EP 0 354 893 each of which is fully incorporated herein by reference.

Polymerization Processes

The branched ethylene-propylene of the present invention may be produced using the catalysts described above in any process including gas, slurry, suspension or solution phase processes. Additionally, combinations of the above reactor types in multiple, series reactors and/or multiple reaction conditions and/or multiple catalyst configurations are explicitly intended.

In the preferred embodiment, this invention is directed toward the polymerization of ethylene and propylene in a slurry or solution phase polymerization process, particularly a solution polymerization process.

Typically in a gas phase polymerization process a continuous cycle is employed wherein one part of the cycle of a reactor, a cycling gas stream, otherwise known as a recycle stream or fluidizing medium, is heated in the reactor by the heat of polymerization. The recycle stream usually contains one or more monomers continuously cycled through a fluidized bed in the presence of a catalyst under reactive conditions. This heat is removed in another part of the cycle by a cooling system external to the reactor. The recycle stream is withdrawn from the fluidized bed and recycled back into the reactor. Simultaneously, polymer product is withdrawn from the reactor and new or fresh monomer is added to replace the polymerized monomer. (See for example U.S. Patent Nos. 4,543,399; 4,588,790; 5,028,670; 5,352,749; 5,405,922, and 5,436,304 all of which are fully incorporated herein by reference.)

A slurry polymerization process generally uses pressures in the range of from about 1 to about 500 atmospheres or even greater and temperatures in the

range of from -60°C to about 280°C . In a slurry polymerization, a suspension of solid, particulate polymer is formed in a liquid or supercritical polymerization medium to which ethylene, propylene and comonomers and often hydrogen along with catalyst are added. The medium employed should be liquid under the conditions of polymerization and relatively inert. The liquid employed in the polymerization medium can be an inert hydrocarbon solvent or diluent. For example, an alkane or a cycloalkane such as hexane or isobutane can be used. In a preferred embodiment, hexane or propylene monomer serves as the polymerization diluent.

Preferably, the ethylene monomers, the propylene monomers and the inert hydrocarbon solvent or diluent comprise no more than 90 percent of the total contents of the reactor. More preferably, they comprise no more than 80 percent of the total contents of the reactor. Most preferably, the ethylene monomers, the propylene monomers and the inert hydrocarbon solvent or diluent comprise no more than 70 percent of the total contents of the reactor. In a preferred embodiment, the ethylene monomers, the propylene monomers and the inert hydrocarbon solvent or diluent comprise at least 50 percent of the total contents of the reactor.

Also, the ratio in the reactor of the ethylene and propylene monomers to the inert hydrocarbon solvent or diluent in the reactor feed is preferably less than 2.0. More preferably, the ratio is less than 1.0. Still more preferably, it is less than 0.8. Most preferably, the ratio in the reactor of the ethylene and propylene monomers to the inert hydrocarbon solvent or diluent in the reactor feed is less than 0.5.

Preferably, the polymerization is carried out using a pressure of from about 200 kPa to about 7,000 kPa at a temperature in the range of from about 50°C to about 180°C .

More preferably, the polymerization is carried out at a temperature in the range of from about 50°C to about 130°C . Most preferably, the polymerization is carried out at a temperature in the range of from 60°C to 110°C .

The polymerization may be conducted in batch, semi-batch or continuous mode and the entire polymerization may take place in one reactor or the polymerization may be carried out in a series of reactors. Preferably, the polymerization is carried out in continuous mode.

5 The reaction time for the polymerization of the present invention will depend upon the catalyst system and reaction conditions.

The above-described temperatures, reaction times and other conditions are considered suitable ethylene-propylene polymerization conditions for the purposes of this invention.

10 Hydrogen may be added to the polymerization system as a molecular weight regulator in the first and/or subsequent reactors depending upon the particular properties of the product desired and the specific metallocenes used. When metallocenes having different hydrogen responses are used, the addition of hydrogen will affect the molecular weight distribution of the polymer product accordingly. Hydrogen may also affect the distribution of branching.

15 For preparation of the branched ethylene-propylene polymer, preactivation of the metallocene may be advantageous. For example, it is widely known in the art that preactivation of the metallocene with alumoxane before addition to a continuous solution-phase reactor yields higher activities than continuous addition of metallocene and activator in two separate streams. Furthermore, it may be advantageous to control precontacting time to maximize catalyst effectiveness, e.g., avoiding excessive aging of the activated catalyst composition.

INDUSTRIAL UTILITY

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The branched ethylene-propylene polymers of the present invention exhibit improved melt properties, such as shear thinning, elasticity, melt strength and low viscosity. The branched ethylene-propylene polymers of the present invention are useful in a variety of applications, including hot melt adhesives, elastic compositions, modifiers and molded products.

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In order that the invention may be more readily understood, reference is made to the following examples, which are intended to illustrate the invention but not to limit the scope thereof.

5 **EXAMPLES**

General

 Liquids were measured into the reactor feed tanks using calibrated sight glasses. High purity (>99.5%) hexane was purified by passing first through basic
10 alumina activated at high temperature in nitrogen, followed by molecular sieve activated at high temperature in nitrogen. Polymerization grade ethylene was supplied directly in a nitrogen-jacketed line and used without further purification, and propylene was purified by passing it through activated basic alumina and molecular sieves. Dimethylanilinium tetrakis(perfluoroaryl)borate [DMAH]⁺
15 [(C₆F₅)₄ B]⁻ was obtained from Boulder Scientific Co., Mead, Colorado.

 Propylene was measured into the reactor through a calibrated container. To ensure the reaction medium was well mixed, a flat-paddle stirrer rotating at 750 rpm was used. Polymerization was performed in 0.5 liter (continuous) Zipperclave reactor equipped with a water jacket for temperature control. The
20 reactors were first cleaned by heating to 120°C in toluene to dissolve any polymer residues, then cooled and drained. Next, the reactor was heated using jacket water at 110°C and the reactor was purged with flowing nitrogen for a period of >30 minutes.

25 **Catalysts**

 All catalyst preparations were performed in an inert atmosphere with <1.5 ppm H₂O content. The metallocenes used in the syntheses were obtained from internal sources. The catalysts, Dimethylsilyl bis(2-methyl-indenyl) ZrMe₂ ("Catalyst A") and Dimethylsilyl bis(indenyl)hafnium dimethyl ("Catalyst B")
30 were preactivated with [DMAH]⁺ [(C₆F₅)₄ B]⁻. Catalysts for the continuous

reactions were metered continuously into the reactor from a stainless steel supply bomb (pressurized at 100 psig) using an HPLC pump.

Continuous Polymerization

5 A fully instrumented 0.5 liter Zipperclave reactor was used for continuous reaction experiments. DMAH-activated catalysts were used in these reactions. Each run utilized 30 mg of Catalyst A or Catalyst B (1:1.3 molar DMAH) in 100 ml toluene, preactivated 15 minutes before loading into the feed bomb for injection/metering by the HPLC pump. Hexane, propylene and ethylene feeds
10 were premixed in an 18 liter feed tank. Ethylene concentrations were controlled by controlled addition of an ethylene partial pressure above that of the propylene/hexane mix. After ethylene addition, the feed tank was closed, then pressurized with nitrogen to 200 psig. A positive displacement pump was used to meter the feed into the reactor and to raise the pressure sufficiently to prevent
15 bubbling of the reaction medium at reaction temperatures. In this way, liquid-full reaction was accomplished. Reactor pressure was controlled using a downstream backpressure regulator. At the highest pump setting, a residence time of approx. 2 minutes was obtained using the 0.5 liter reactor body.

GPC/DRI and GPC/Vis Analysis

20 The molecular weight and MWD of the polymers were measured by a Waters 150-C ALC/GPC. Branching levels were measured by GPC/Vis and are reported as g' at each molecular weight in the GPC trace. Relating the measured g' to branched structure requires the application of Zimm-Stockmayer theory, which
25 assumes a random distribution of branch sizes for each population of branched structures (singly, doubly, triply branched, etc.) at each molecular weight. See B.H. Zimm and W.H. Stockmayer, J. Chem. Phys. 17, 1301 (1949).

Examples 1-24

30 Experiments were run using continuous polymerization conditions. The data from these runs is presented in Table 1.

Table 1. Continuous Reactor Used to Synthesize Branched High-C₃ EP Compositions

Example	Cat.	Pump Rate (rel.)	Temp (C)	Ethylene Partial Pressure (psi)	Feed C ₃ Flow (g/min)	Yield g/min	Mn*	Mw*	Mz*	Mw/Mn	Mole % Ethylene**	g'(ave)***
1	A	50	90	35	19.27	12.9	4000	10700	21100	2.67	14.38	.660
2	A	25	90	35	19.27	13.65	4430	12400	23500	2.79	15.16	.665
3	A	25	70	35	19.27	10.91	7420	17100	28500	2.30	16.46	.637
4	A	25	70	35	19.27	8.88	13600	28800	44900	2.11	15.44	.631
5	B	50	90	35	19.27	20.7	14300	36100	59800	2.52	14.8	.637
6	B	25	90	35	19.27	10.33	22900	46900	74500	2.04	15.6	.6944
7	B	50	70	35	19.27	18.85	34300	69400	113400	2.02	15.2	.714
8	B	25	70	35	19.27	12.28	41300	81700	136100	1.97	14.0	.797
9	B	50	90	18	19.27	11.39	16900	36000	58000	2.13	11.2	.692
10	B	25	90	18	19.27	8.88	25100	48500	74700	1.93	11.9	.712
11	B	50	70	18	19.27	11.3	38900	75900	121600	1.95	8.8	.798
12	B	25	70	18	19.27	8.99	48100	91000	145400	1.89	9.7	.830
13	B	50	90	13.5	19.27	10.18	12800	32100	57600	2.508	7.8	
14	B	25	90	13.5	19.27	9.57	16300	37500	65000	2.301	7.7	
15	B	50	70	13.5	19.27	10.19	29800	63800	106000	2.141	8.5	
16	B	50	70	13.5	19.27	9.8	46300	93000	158200	2.009	6.4	
17	B	25	70	13.5	19.27	9.38	49700	97600	157300	1.964	6.2	
18	B	25	60	13.5	19.27	8.85	73800	148100	244600	2.007	7.1	
19	A	50	90	13.5	19.27	9.0	5020	10300	18700	2.052	8.0	
20	A	25	90	13.5	19.27	7.73	5300	10600	17800	2.000	8.2	
21	A	50	70	13.5	19.27	10.23	9420	19500	32100	2.070	7.9	
22	A	25	70	13.5	19.27	10.02	12800	25800	41100	2.016	7.0	
23	A	50	55	13.5	19.27	10.16	23100	44300	68800	1.918	9.0	
24	A	25	55	13.5	19.27	9.78	18000	41400	67900	2.300	4.8	

*data from GPC/Vis ** as measured using FTIR *** weight average of molecular weights >Mp

5 While certain representative embodiments and details have been shown for the purposes of illustrating the invention, it will be apparent to those skilled in the art that various changes in the process and products disclosed herein may be made without departing from the scope of the invention, which is defined in the appended claims.

CLAIMS

We claim:

- 5 1. A semi-crystalline, majority propylene composition comprising propylene, ethylene comonomer and, optionally, other comonomers, wherein the total comonomer content of said ethylene-propylene composition is from 5 to 40 mole percent, and further, wherein the weight average branching index g' for the higher molecular weight region of said ethylene-propylene composition is less than 0.95.
- 10 2. The composition of claim 1 wherein the weight average branching index g' for the higher molecular weight region of said ethylene-propylene composition is less than 0.90.
- 15 3. The composition of claim 1 wherein the weight average branching index g' for the higher molecular weight region of said ethylene-propylene composition is less than 0.85.
- 20 4. The composition of claims 1-3 wherein said one or more other comonomers are selected from the group consisting of C_4 - C_{20} α -olefins, geminally disubstituted monomers, C_5 - C_{25} cyclic olefins, C_8 - C_{25} styrenic olefins, and lower carbon number (C_3 - C_8) alkyl substituted analogs of the cyclic and styrenic olefins.
- 25 5. The composition of claim 4 wherein said one or more other comonomers comprise from 3 to 25 mole percent of said ethylene-propylene composition.
- 30 6. A process for producing a branched ethylene-propylene composition comprising:
- a) contacting propylene monomers and ethylene monomers in a reactor with an inert hydrocarbon solvent or diluent and a catalyst composition comprising one or more single site catalyst compounds capable of producing an ethylene-propylene polymer at a temperature from about 50°C to about 180°C, wherein the ratio

in the reactor of said propylene and ethylene monomers to said inert hydrocarbon solvent or diluent is less than 2.0, and further, wherein said propylene and ethylene monomers and said inert hydrocarbon solvent or diluent comprise no more than 90 percent of the total contents of said reactor; and

- b) recovering a branched ethylene-propylene composition, wherein the weight average branching index g' for the higher molecular weight region of said ethylene-propylene composition is less than 0.95.

7. The process of claim 6 wherein said one or more single site catalyst compounds comprise one or more metallocene catalyst compounds.

8. The process of claim 7 wherein step a) is conducted by a process in which said propylene monomers are contacted with said one or more metallocene catalyst compounds activated by an alumoxane cocatalyst or non-coordinating anion precursor.

9. The process of claims 7-8 wherein said one or more metallocene catalyst compounds are selected from the group consisting of substituted bridged bis-indenyl zirconocenes and hafnocenes.

10. The process of claim 9 wherein said catalyst composition consists of a substituted bridged bis-indenyl zirconocene activated with a non-coordinating anion precursor.

11. The process of claim 10 wherein said bridged bis-indenyl zirconocene is dimethylsilyl (2-methyl-4-phenylindenyl) zirconium dichloride.

12. The process of claims 6-11 wherein step a) is conducted by a process in which said propylene and ethylene monomers and said inert hydrocarbon solvent or diluent comprise no more than 80 percent of the total contents of said reactor.
- 5 13. The process of claims 6-12 wherein said propylene and ethylene monomers in step a) are contacted at a temperature from 50°C to 130°C.
14. The process of claims 6-13 wherein the ratio in the reactor of said propylene and ethylene monomers to said inert hydrocarbon solvent or diluent is
10 less than 1.0.
15. The process of claims 6-14 wherein said process is continuous.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 99/29787

A. CLASSIFICATION OF SUBJECT MATTER IPC 7 C08F210/06 C08F210/16		
According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED Minimum documentation searched (classification system followed by classification symbols) IPC 7 C08F		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched		
Electronic data base consulted during the international search (name of data base and, where practical, search terms used)		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 384 431 A (HIMONT INC) 29 August 1990 (1990-08-29) cited in the application page 3, line 33 - line 44; claims; table 1	1-5
X	WO 91 17194 A (EXXON CHEMICAL PATENTS INC) 14 November 1991 (1991-11-14) claims	1-5
X	WO 97 01586 A (MUSKENS BERNARDUS JOHANNA ;RENKEMA JACOB (NL); DSM NV (NL); OOSTER) 16 January 1997 (1997-01-16) page 5, line 3 - line 13; claims	1-7, 12-15
X	WO 94 07930 A (EXXON CHEMICAL PATENTS INC) 14 April 1994 (1994-04-14) page 31, line 2; claims	1-7, 12-15
-/--		
<input checked="" type="checkbox"/> Further documents are listed in the continuation of box C. <input checked="" type="checkbox"/> Patent family members are listed in annex.		
* Special categories of cited documents :		
A document defining the general state of the art which is not considered to be of particular relevance *E* earlier document but published on or after the international filing date *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) *O* document referring to an oral disclosure, use, exhibition or other means *P* document published prior to the international filing date but later than the priority date claimed		*T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention *X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone *Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art. *&* document member of the same patent family
Date of the actual completion of the international search 11 April 2000		Date of mailing of the international search report 20/04/2000
Name and mailing address of the ISA European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016		Authorized officer Kaumann, E

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 99/29787

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 98 33823 A (PENN STATE RES FOUND) 6 August 1998 (1998-08-06) abstract; claim 8; example 41	1-6, 12-15
A	EP 0 855 413 A (JAPAN SYNTHETIC RUBBER CO LTD) 29 July 1998 (1998-07-29) claims; examples; tables	6-15
A	WO 97 00286 A (EXXON CHEMICAL PATENTS INC) 3 January 1997 (1997-01-03) page 12, line 17 -page 13, line 13; claims	1-15
P,X	WO 99 29742 A (EXXON CHEMICAL PATENTS INC) 17 June 1999 (1999-06-17) page 4, line 18; claims	1-15

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 99/29787

Patent document cited in search report	A	Publication date	Patent family member(s)	Publication date
EP 0384431	A	29-08-1990	US 5047485	A 10-09-1991
			AT 114677	T 15-12-1994
			AU 616103	B 17-10-1991
			AU 4994390	A 30-08-1990
			CA 1339476	A 23-09-1997
			CN 1045107	A, B 05-09-1990
			DE 69014348	D 12-01-1995
			DE 69014348	T 20-04-1995
			DK 384431	T 16-01-1995
			ES 2064503	T 01-02-1995
			JP 2298536	A 10-12-1990
			JP 2744317	B 28-04-1998
			KR 145323	B 15-07-1998
			NO 900738	A 22-08-1990
			PT 93206	A 31-08-1990
			RU 2036931	C 09-06-1995
			ZA 9000911	A 28-12-1990
<hr/>				
WO 9117194	A	14-11-1991	AU 7875791	A 27-11-1991
			US 5504171	A 02-04-1996
			US 5514761	A 07-05-1996
<hr/>				
WO 9701586	A	16-01-1997	NL 1000687	C 31-12-1996
			AU 6244596	A 30-01-1997
			BR 9609483	A 02-03-1999
			CA 2225742	A 16-01-1997
			EP 0835271	A 15-04-1998
			JP 11509881	T 31-08-1999
			US 5999210	A 07-12-1999
<hr/>				
WO 9407930	A	14-04-1994	AU 4928993	A 26-04-1994
			CA 2145635	A 14-04-1994
			EP 0662980	A 19-07-1995
			JP 8502303	T 12-03-1996
<hr/>				
WO 9833823	A	06-08-1998	AU 6147398	A 25-08-1998
<hr/>				
EP 0855413	A	29-07-1998	US 5914372	A 22-06-1999
<hr/>				
WO 9700286	A	03-01-1997	US 5766713	A 16-06-1998
			DE 69602950	D 22-07-1999
			DE 69602950	T 13-01-2000
			EP 0843702	A 27-05-1998
<hr/>				
WO 9929742	A	17-06-1999	NONE	